

Section II. REMARKS

This addresses the position of the examiner set forth in the Advisory Action mailed March 12, 2007 in this application, and provides supplementary remarks in rebuttal of the maintained rejections, showing the patentable distinction of applicants' pending claims 1-8, 11-14, 16-23, 27-31, 37-41, 43, 45-78, 80-93 and 97-112.

The examiner in the March 12, 2007 Advisory Action has raised a new round of rejection in her 112, first paragraph rejection of claims 1-8, 11-14, 16-23, 27-31, 43 and 45-64.

This written description rejection is now based on the examiner's contention that the specification does not show that the inventors had possession of making a Ru layer "with any co-reactant gas at the time of the invention... absent a working example in the disclosure showing that the applicants had possession of making a ruthenium metal layer using any co-reactant gas, as is claimed." She then states that "Table 2 ...only shows the layer being made with oxygen and hydrogen."

The examiner's rejection ignores the disclosure at paragraph [0006] of prior art CVD deposition of ruthenium "using a gasified ruthenium source and a co-reactant gas." Applicants' broadly claimed invention, as set forth in claim 1, is:

1. A method for depositing a ruthenium thin film onto a substrate, said method comprising:

(a) depositing a nucleation layer comprising ruthenium metal onto the substrate by chemical vapor deposition, wherein the nucleation layer is deposited using a first ruthenium precursor/co-reactant gas mixture having greater than about 30 mole percent of the co-reactant gas, under nucleation layer CVD conditions including a temperature of from about 250°C to about 340°C and a ruthenium precursor gas flow rate that is sufficient to maintain a surface reaction rate-limited deposition; and

(b) depositing an upper layer comprising ruthenium metal onto the nucleation layer by chemical vapor deposition, wherein the upper layer is deposited using a second ruthenium precursor/co-reactant gas mixture having less than 50 mole percent of the co-reactant gas under upper layer CVD conditions, including a ruthenium precursor gas flow rate that is less than that needed to maintain a surface reaction rate-limited deposition.

Applicants have discovered a process regime in which the nucleation layer can be formed at specific temperature and flow rate (surface reaction rate-limited deposition) conditions, with greater than about 30 mol percent co-reactant gas, followed by upper layer deposition under sub-surface reaction rate-limited deposition conditions, with less than about 50 mol percent co-reactant gas.

The applicable law is clear that an example is not required of every conceivable co-reactant gas species, when co-reactant gas species are known in the prior art. See, for example, MPEP 2163

"The description need only describe in detail that which is new or not conventional. See *Hybritech v. Monoclonal Antibodies*, 802 F.2d at 1384, 231 USPQ at 94; *Fonar Corp. v. General Electric Co.*, 107 F.3d at 1549, 41 USPQ2d at 1805 (source code description not required). This is equally true whether the claimed invention is directed to a product or a process. ... See also *Capon v. Eshhar*, 418 F.3d 1349, 1357, 76 USPQ2d 1078, 1085 (Fed. Cir. 2005)"

Further, in light of the examiner's remark conceding that the applicants' disclosure shows "the layer being made with oxygen and hydrogen" (March 12, 2007 Advisory Action, page 2, lines 15-16), it is to be noted that the examiner's 112, first paragraph rejection has not only been applied to applicant's broad claim 1, but it also has been asserted against claims reciting such oxygen and/or hydrogen species, including:

- claim 12 ("wherein the first co-reactant gas comprises oxygen"),
- claim 38 ("wherein the second co-reactant gas comprises oxygen"),
- claim 39 ("wherein the second co-reactant gas comprises an oxygen: hydrogen gas mixture"),
- claim 40 ("wherein the oxygen: hydrogen gas mixture has a mole ratio in a range of about 1:1 to about 1:3"),
- claim 58 ("wherein from about 80 mole% to about 90 mole% of the first ruthenium precursor/co-reactant gas mixture is oxygen"),
- claim 59 ("wherein from about 80 mole% to about 95 mole% of the first ruthenium precursor/co-reactant gas mixture is oxygen and from about 1 mole% to about 20 mole% of the second ruthenium precursor/co-reactant gas mixture is oxygen"),
- claim 63 ("wherein the second co-reactant gas is a mixture of oxygen and hydrogen"), and
- claim 64 ("wherein each co-reactant gas is individually selected from the group consisting of oxygen, hydrogen, steam, nitrous oxide, ozone, carbon monoxide, common dioxide, and mixtures of oxygen and hydrogen").

In this respect, it is further pointed out that the examiner has not applied such 112, first paragraph rejection against any of the following claims containing similar recitals to the rejected claims identified above:

- claim 65 ("a nucleation layer of ruthenium precursor/co-reactant gas mixture, the mixture having at least a 30 mole% oxygen content"),
- claim 69 ("wherein the co-reactant gas is oxygen"),
- claim 77 ("the co-reactant gas is oxygen and is present in a concentration of from about 80 mole% to about 95 mole%"),
- claim 78 (dependent from claim 77),
- claim 80 (dependent from claim 65), claim 80 (dependent from claim 65),
- claim 81 ("wherein the co-reactant gas comprises oxygen"),
- claim 107 ("the co-reactant gas is oxygen" and "from about 1 mole% to about 10 mole% of the second ruthenium precursor/co-reactant gas mixture comprises oxygen"),
- claim 108 ("wherein the second co-reactant gas comprises an oxygen:hydrogen gas mixture"), and
- claim 109 (dependent from claim 108, reciting "wherein the ratio of oxygen to hydrogen is from about 1:1 to about 1:3").

It therefore is apparent that the examiner's 112, first paragraph rejection is incorrect generally as well as specifically, that it has been applied inconsistently to some claims and not to others containing the same recitals, and that the examiner has in fact applied the 112, first paragraph rejection against claims reciting co-reactant species that the examiner has in fact acknowledged as being disclosed! The foregoing shows that the 112, first paragraph rejection has been improperly asserted, and should be withdrawn.

The examiner in the March 12, 2007 Advisory Action has maintained the 35 USC 102 rejection based on Jin, specifically maintaining that such reference "meets the recitations of the claim 65 at least as broadly as they are recited," despite the fact that applicants have clearly shown that Jin does not teach repetition of the process for forming the layer, or use of the same process conditions as in the applicants' claimed invention. The examiner has cited Jin at column 4, lines 14-44. In applicants' response filed February 26, 2007 in reply to the prior Advisory Action, the entire cited text of Jin at column 4, lines 14-44 was set out, and again is reproduced below:

"In one embodiment, the present invention is directed to a method of forming a ruthenium seed layer on a substrate comprising the steps of vaporizing a ruthenium-containing compound; introducing the vaporized ruthenium-containing compound into a CVD apparatus; introducing oxygen into the CVD apparatus; maintaining an oxygen rich environment in a process chamber of the CVD apparatus for the initial formation of a ruthenium oxide seed layer; depositing the ruthenium oxide seed layer onto the substrate by chemical vapor deposition; and annealing the deposited

ruthenium oxide seed layer in a gas ambient forming a ruthenium seed layer. Generally, an oxygen to ruthenium ratio from about 1:1 to 100:1 is used. The ratio may also be 14:1. The ruthenium-containing compound is heated to about 200° C. to about 400° C. Examples of these compounds are ruthenium bis-(ethylcyclopentadienyl) and ruthenium octanedionate. The vapor deposited ruthenium seed layer is annealed in an H₂/N₂, H₂ or H₂/Ar gas environment at about 200° C. to about 600° C. Hydrogen gas may comprise about 10% to 100% of the ambient. Representative examples of the substrate include silicon, silicon dioxide, titanium nitride, titanium aluminum nitride, tantalum nitride, tantalum pentoxide and barium strontium titanate. One object of this embodiment is to provide a ruthenium seed layer with a structure of RuO_x prior to annealing of the seed layer, where x is 2, and RuO_x contains about 60% oxygen and after annealing of the seed layer, a ruthenium seed layer with a structure RuO_y is formed, where y is less than 2, and contains less than about 20% oxygen. A ruthenium seed film deposited in accordance with this method may have a thickness of about 100 Å or less." (Jin et al., column 4, lines 14-44)

Specifically, the examiner has asserted that column 4, lines 21-23 discloses that Jin "continuously repeats this deposition" whereas in fact these lines simply disclose "depositing the ruthenium oxide seed layer onto the substrate by chemical vapor deposition," and in no way describe or in any way suggest any repetition.

The examiner in connection with such assertion has further contended that column 4, lines 42-44 of Jin relates to such repetition "until the layer of desired thickness is formed" (page 3, lines 3-4 of the March 12, 2007 Advisory Action), whereas in fact column 4, lines 42-44 simply states that "[A] ruthenium seed film deposited in accordance with this method may have a thickness of about 100 Å or less.

Claim 65 is set out below:

65. A method for depositing a ruthenium thin film onto a substrate, said method comprising:

(a) depositing a nucleation layer comprising ruthenium onto the substrate by chemical vapor deposition, wherein the nucleation layer is deposited from a nucleation layer ruthenium precursor/co-reactant gas mixture, the mixture having at least a 30 mole % oxygen content, in an oxidizing environment under nucleation layer CVD conditions;

(b) deoxygenating the so formed nucleation layer in a reducing environment, in the absence of the ruthenium precursor/co-reactant gas mixture; and

(c) sequentially repeating steps (a) and (b) until the ruthenium thin film of desired thickness is deposited onto the substrate.

It is apparent that there is no anticipatory disclosure in Jin of the presently claimed process of claim 65, and that the rejection has no substantive basis in fact. The 102 rejection therefore should be withdrawn.

The examiner in the March 12, 2007 Advisory Action also has maintained her rejection of claims 1-8, 11-14, 16-23, 27-31, 37-41, 43 and 45-64 based on Wade in view of Shinamoto.

It is fundamental to a proper 103 rejection of claims that an examiner must present a convincing line of reasoning supporting the rejection. MPEP 2144 ("Sources of Rationale Supporting a Rejection Under 35 U.S.C. 103"), citing *Ex parte Clapp*, 227 USPQ 972 (Bd. Pat. App. & Inter. 1985) (examiner must present convincing line of reasoning supporting rejection).

In response to applicant's argument that Wade teaches away from using a ruthenium seed layer and using CVD, that Shinamoto fails to teach CVD of a ruthenium metal seed layer, and that proper motivation to combine the two references is lacking, the examiner has contended that Wade teaches forming a ruthenium film by chemical vapor deposition, citing column 4, line 59 to column 5, line 13, and that the purpose of Wade is to use CVD to create a ruthenium seed layer (the examiner citing the title, "Chemical vapor deposition of ruthenium films for metal electrode applications" as the basis for such assertion), that Wade discloses depositing a ruthenium oxide seed layer, citing column 5, lines 14-37, and that the examples and tables of Wade anticipate the process conditions given in the applicant's claims.

Shinamoto has been cited by the examiner "to show that the ruthenium metal layer of Wade is useful as a seed layer" (page 3, lines 16-17).

The examiner has cited the motivation for combination of the Wade and Shinamoto references as being "to use a ruthenium metal layer as a seed layer in order to control the oxygen content in the film - the entire film including the separate layers and their interaction with the substrate (column 4 lines 3-14 and columns 5 and 6 lines 66-17 [sic] of Shinamoto, also see figures)."

As was stated in the applicants' prior response, the hypothesized "motivation... to control the oxygen content of the film" is a motivation that finds no derivative or supportive basis in either of the Wade et al. or Shinamoto et al. references, and begs the question why, *a priori*, one would be thus motivated, since Wade et al. contain no statement, disclosure, or any description that in any way suggests that the ruthenium films disclosed in Wade et al. are in any way uncontrolled or in any way deficient or unsuitable in respect of oxygen content, such that there would be a need to look elsewhere, e.g., in Shinamoto et al., to resolve such "uncontrolled oxygen content" problem.

Contrarily, Wade et al. assert the effectiveness and suitability of the films and processes they disclose.

For example, Wade et al. disclose at column 2, lines 13-18 that:

"The prior art is deficient in the lack of effective means of depositing pure thin ruthenium films on a substrate using a chemical vapor deposition source that is liquid at room temperature and where deposition temperature occurs in the kinetic-limited temperature range. The present invention fulfills this long-standing need and desire in the art." (Wade et al., column 2, lines 13-18)

The clear import of such statements is that Wade et al. are effective in depositing pure ruthenium films on a substrate, in a manner fulfilling "long-standing need and desire in the art." There is accordingly no basis for attributing to Wade et al. any defect, deficiency or inadequacy in respect of controlling oxygen content in the film that is deposited in accordance with the disclosed process of such reference.

Shinamoto et al. disclose a process that "efficiently forms a ruthenium film with good conformality" (Shinamoto et al., Abstract, line 9), and such reference does not contain any disclosure that would suggest that Wade et al.'s process produces a film with an "uncontrolled oxygen content" problem that would require fixing by somehow extracting specific process features from the Shinamoto et al. process and importing same into the Wade et al. process.

The "uncontrolled oxygen content" problem therefore is *simply a construct without any tenable or supporting basis in either the references*, which has been posited as the basis for an allegation

of obviousness of applicants' claims. It is clear, however, from the foregoing, that no such motivation is present.

Since, as stated in MPEP 2143, a proper *prima facie* case of obviousness under 35 USC 103 (a) requires "some suggestion or motivation, either in the references themselves or in the knowledge generally available to one of ordinary skill in the art, to modify the reference or to combine reference teachings," and since such suggestion or motivation is absent in the present circumstance, it is apparent that the rejection of claims 1-8, 11-14, 16-23, 27-31, 37 and 41, 43 and 45-64 is without basis and should now be withdrawn.

The examiner now has stated that Shinamoto is used to show that the ruthenium metal layer of Wade is useful as a seed layer, and "that Shinamoto teaches that the layers of Wade et al. may be used to make a seed layer so that the entire film of a device has controlled oxygen content" (March 12, 2007 Advisory Action, page 3, line 21 to page 4, line 1). In fact, Shinamoto contains no such disclosure of Wade et al., and does not even mention such reference. The examiner's statement that Shinamoto addresses Wade's layers simply has no basis in the actual disclosure of Shinamoto.

Thus, no actual basis for combination has been shown by the examiner, and none is in any way apparent from the references themselves. Further, the examiner's assertion that "Wade teaches the limitations of the claims" (March 12, 2007 Advisory Action, page 3, line 11) is not accurate. Claim 1, for example, is set out below:

1. A method for depositing a ruthenium thin film onto a substrate, said method comprising:

(a) depositing a nucleation layer comprising ruthenium metal onto the substrate by chemical vapor deposition, wherein the nucleation layer is deposited using a first ruthenium precursor/co-reactant gas mixture having greater than about 30 mole percent of the co-reactant gas, under nucleation layer CVD conditions including a temperature of from about 250°C to about 340°C and a ruthenium precursor gas flow rate that is sufficient to maintain a surface reaction rate-limited deposition; and

(b) depositing an upper layer comprising ruthenium metal onto the nucleation layer by chemical vapor deposition, wherein the upper layer is deposited using a second ruthenium precursor/co-reactant gas mixture having less than 50 mole percent of the co-reactant gas under upper layer CVD conditions,

including a ruthenium precursor gas flow rate that is less than that needed to maintain a surface reaction rate-limited deposition.

Relative to such claimed method, Wade fails to teach or in any way suggest deposition of a nucleation layer by CVD under surface reaction rate-limited deposition conditions¹, followed by deposition of an upper layer by CVD under non-surface reaction rate-limited deposition conditions ("CVD conditions, including a ruthenium precursor gas flow rate that is less than that needed to maintain a surface reaction rate-limited deposition"- applicant's claim 1, paragraph (b)).

In Example 6 (column 9, lines 28-32), Wade discloses that

"[F]or good step coverage and conformality, the CVD process needs to be operated below the "knee" in the kinetic-limited regime. The "knee" is defined as the transition point between the mass-transfer limited regime and the kinetic-limited regime."

The kinetic-limited regime is defined in Wade at column 5, lines 46-51 as "the range of deposition temperatures over which the deposition rate of a chemical vapor deposition film is limited by the kinetics of the chemical reactions at the substrate surface, typically characterized by a strong dependence of deposition rate on temperature."

Thus, Wade teaches that when CVD is employed for deposition, it is in the "kinetic-limited regime." Accordingly, if a seed layer were to be deposited by CVD as proposed by the examiner, followed by deposition of ruthenium metal on the seed layer by CVD, as also proposed by the examiner, then consistent with the teachings of Wade, both depositions (of the seed layer and the over layer) would be in the "kinetic-limited regime," opposite to the applicant's process in which the upper layer of ruthenium is deposited under non-surface reaction rate-limited deposition conditions ("CVD conditions, including a ruthenium precursor gas flow rate that is less than that needed to maintain a surface reaction rate-limited deposition"- applicant's claim 1, paragraph (b)).

¹ The term "surface reaction rate-limited depositions" is specified at paragraph [0031] of the present application as occurring "when, for a particular temperature and co-reactant gas, the precursor gas is transported to the surface faster than it can react on the surface... the rate of film deposition is controlled by the reaction kinetics of the surface and is independent of mass transport of the precursor to the surface."

The examiner has based the motivation to combine Wade and Shinamoto on the disclosure at column 4, lines 3-14 of Shinamoto:

Additionally, the chemical vapor deposition should preferably be preceded by a step of forming a seed layer comprised of at least one metal selected from the group consisting of ruthenium, platinum, iridium, rhodium, osmium, palladium, cobalt, iron, and alloys thereof.

The above-mentioned method makes it possible to control the amount of oxygen adsorbed on the surface inside the hole. The process of the present invention is explained more fully below in which the organoruthenium compound is bis(ethylcyclopentadienyl)ruthenium ($\text{Ru}(\text{C}_2\text{H}_5\text{C}_5\text{H}_4)_2$ or $\text{Ru}(\text{EtCp})_2$) and the oxygen absorption preventing gas is tetrahydrofuran (THF).

- column 4, lines 3-14 of Shinamoto

and the disclosure at column 5, line 66 to column 6, line 17 of Shinamoto:

The foregoing suggests that the partial pressure of THF gas controls the oxygen adsorption density and the distribution of oxygen density in the hole. It is considered that when the partial pressure of THF gas is small, the oxygen supplied is mostly adsorbed by the patterned flat part or the upper inside of the hole and hence does not reach deep inside the hole. Thus, it is further considered that the oxidation decomposition reaction of the organoruthenium compound, which is limited by the amount of oxygen adsorbed, proceeds, thereby aggravating conformality at the bottom of the hole. On the other hand, it is considered that when the partial pressure of THF is high, THF gas sufficiently adsorbs to the surface of the Ru seed layer, thereby preventing the adsorption of oxygen but permitting the diffusion of oxygen to the bottom of the hole, and a constant low density of oxygen adsorption is realized. This causes good conformality at the bottom of the hole. In addition, it is considered that the density of oxygen adsorption decreases with an increasing partial pressure of THF gas, and, hence, the film-forming rate also decreases as shown in FIG. 8(b).

The foregoing in fact provides no basis for importing Wade's teachings into Shinamoto, as proposed by the examiner, since Shinamoto teaches to form the Ru seed layer by sputtering, not chemical vapor deposition. See, for example, the following disclosures in Shinamoto:

"On the inside of the hole, a Ru seed layer (1-2 nm thick) was formed by long throw sputtering" – column 5, lines 49-51 of Shinamoto

"The procedure starts with the formation of a Ru seed layer (20 nm thick) by sputtering, and then the desired film is formed." – column 7, lines 35-36 of Shinamoto

"The procedure begins with the formation of a Ru seed layer (20 nm thick) by sputtering, and then the desired film is formed." – column 8, lines 64-66 of Shinamoto

"First, a seed layer of Ru is formed on the substrate by sputtering." – column 11, lines 47-48 of Shinamoto

"With the resist removed, long throw sputtering is performed to form a lower seed layer 4 of Ru" – column 15, lines 7-9 of Shinamoto

"Subsequently, an upper seed layer 8 of Ru is formed on the oxide dielectric material 6 by long throw sputtering" – column 18, lines 45-46

Thus, Shinamoto teaches away from the applicant's invention as claimed, by Shinamoto's use of sputtering, and Shinamoto is devoid of any teaching or suggestion of using a non-sputtering technique for seed layer formation.

In this respect, it is to be noted that Wade teaches the use of a non-CVD technique, physical vapor deposition, as most preferred for seed layer formation. See, for example,

- column 10, lines 42-45 of Wade et. al. ("The lower activation energies and higher deposition rates on PVD Ru highlight the importance of using a PVD Ru seed layer as a substrate for CVD Ru growth");
- column 14, lines 44-45 of Wade et. al. ("[U]sing the same process conditions, the surface morphology was improved by using a thin PVD Ru seed layer...."); and
- column 16, lines 12-13 of Wade et. al. ("By depositing CVD Ru onto a PVD Ru seed layer, the film roughness and step coverage can be greatly reduced").

Since sputtering is a physical vapor deposition process, the examiner's hypothetical synthesis of Wade and Shinamoto (which applicants again note has no tenable basis, either in the references themselves or in the general knowledge of the art applicable to the field of the invention) would necessitate utilizing a physical vapor deposition process for seed layer formation, particularly since Wade et al. in Table 1 at column 7, line 18 thereof, under the heading "Current Best Known Method" specifies physical vapor deposition for the seed layer ("requires PVD seed").

Accordingly, there is no way that the references of Wade and Shinamoto can be aggregated to yield the applicants' claimed invention as broadly set forth in claim 1, since the combination lacks any derivative basis for deposition of a nucleation layer by CVD under surface reaction rate-limited deposition conditions, followed by deposition of an upper layer by CVD under non-surface reaction rate-limited deposition conditions ("CVD conditions, including a ruthenium

precursor gas flow rate that is less than that needed to maintain a surface reaction rate-limited deposition"- applicant's claim 1, paragraph (b)).

Since it is an elemental requirement of a proper 103 rejection that all claim limitations must be taught or suggested by the prior art to establish *prima facie* obviousness (see MPEP 2143.03 and *In re Royka*, 490 F.2d 981, 180 USPQ 580 (CCPA 1974)), it is evident that the 103 rejection of applicants' pending claims based on Wade et al. in view of Shinamoto et al. has no substantive basis. It therefore is requested that such rejection be withdrawn.

The foregoing supplements the applicants' position of record.

The examiner therefore is requested to take cognizance of the foregoing, and to formally allow the application.

Concurrent Filing of Notice of Appeal

Enclosed and concurrently submitted herewith is a Notice of Appeal, appealing from the final rejection of claims in the November 7, 2006 Office Action.

Petition for Two Months Extension of Time (37 CFR 1.136)

Petition hereby is made under the provisions of 37 CFR 1.136 for a two months extension of time, thereby extending to May 7, 2007 the deadline of the period for reply. It is noted that a one-month extension of time under 37 CFR 1.136 was obtained in the February 26, 2007 Response to the January 26, 2007 Advisory Action in this application. Payment of the appertaining one-month extension fee under 37 CFR 1.17 (a) (1) of \$120 was made at that time.

Accordingly, the additional extension fee payment of \$900, to yield the extension fee of \$1020 specified in 37 CFR 1.17 (a) (3) for a full three-month extension of time, is enclosed by the accompanying Credit Card Authorization Form directing charging of such additional amount of \$900 to the credit card identified in the Form, together with the fee of \$500 specified in 37 CFR 41.20(b)(1) for the Notice of Appeal enclosed and concurrently submitted herewith, for a total charged amount of \$1400.

Authorization also is hereby given to charge the amount of any deficiency in fees or amounts probably payable in connection with the filing and entry of this Response, to Deposit Account No. 08-3284 of Intellectual Property/Technology Law.

CONCLUSION

In view of all of the foregoing, the rejections maintained in the March 12, 2007 Advisory Action have been overcome. Under the requirements of the statute and applicable MPEP provisions, all pending claims 1-8, 11-14, 16-23, 27-31, 37-41, 43, 45-78, 80-93 and 97-112 are patentably differentiated over the cited references. The claims comport with the requirements of 35 USC 112, first paragraph and are otherwise in proper form. It therefore is requested that a Notice of Allowance be issued, consistent with the patentable character of such pending claims.

Respectfully submitted,



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